

3. RESULTS

All figures for this section are presented in the appendices (e.g. Figures A-1 - A-5 are in Appendix A, Figures B-1 - B-32 are in Appendix B)

Quality Control Analysis

Several levels of testing procedure were incorporated to address quality control in the Phase II analysis.

Blanks and Standards

Method blanks were run either on de-ionized, tap, or basin water before the delivery of the media. The purpose of blanks was to ensure the cleanliness of SS analysis. All blanks showed concentrations below 4 mg/L (Figure A-1).

_____The accuracy of the SS procedure was determined from the analysis of laboratory control samples whose true values are known. Standard reference materials (SRM) were the same materials used in the experiments, namely, microsand, Neshaminy silty clay loam, and a 50-50 mix of the sand and Neshaminy. In phase III, diatomaceous-silica will be used as the SRM. Table 3.1 specifies the quality control standard concentrations and the expected recoveries for diatomaceous-silica.

Table 3.1 QA Objectives for Measurements

Measurement	Method	Reporting Unit	Initial Concentration	Standard Deviation	Relative Standard Deviation	Completeness
Suspended Solids	2540D	mg/L	15	5.2	33%	90%
			242	24	10%	90%
			1707	13	0.76%	90%
Settleable Solids	2540F	mg/L	NA	NA	NA	NA

Accuracy is expressed as percent recovery. The formula used to calculate this laboratory QC values for a SRM is:

$$\%R = 100\% \times C_m / C_{\text{srn}} \quad (3-1)$$

where: %R = percent recovery
C_m = measured concentration of SRM
C_{srn} = actual concentration of SRM

Excluding two extremes, the average percent recovery was 83% with media results of 76%, 83% and 88% for sand, mixture and clay, respectively.

Figures A-2 through A-5 show an analysis of the measured standards versus the expected percent recovery (the log linear line in all the graphs) for diatomaceous silica as developed from the values for relative standard deviation in Table 3.1. To plot a comparison versus the relative standard deviation values in Table 3.1, %R was adjusted by subtracting from 100% to get relative percent difference (RPD) values.

Figure A-2 shows RPD for all the media and Figures A-3 through A-5 are media specific. The Neshaminy (Figure A-5) exhibits the best RPD, equivalent to expected recoveries of diatomaceous silica. The mixture (Figure A-4) had several RPD within acceptable limits but for most cases exceeded the limits of diatomaceous silica by up to 45%. The microsand (Figure A-3) exceeded the expected RPD for diatomaceous silica in all but one case.

The microsand was the most difficult media to work with when performing SS, as particles tended to stick to the surfaces of analytical equipment due to water tension. The analysis of microsand produced the most pronounced losses. Neshaminy soil was much easier to analyze (except when the filters began to clog) as the results indicate. Except for one extreme outlier of -189% for a mixture sample (A-4) which represented a gain in mass, all SRM analysis indicated a loss in SS.

Another factor that may have contributed to this error in the SRM was the smaller sample sizes, 125 mL bottles, while Long column sample were 250 to 300 mL and CERGRENE samples were 250 mL for Neshaminy and 960 mL for the microsand and the mixture.

Completeness

The completeness is defined for this study as the ratio of the number of valid measurements to the total number of measurements planned for each parameter. A completeness objective of 90 percent is expected to ensure that sufficient valid data are collected to evaluate the settling velocity distributions. Table 3.2 shows the completeness for critical SS measurements made for all 15 test. The formula used to determine completeness is:

$$\%C = 100\% \times V/T \quad (3-2)$$

where % C = percent completeness
 V = number of measurements judged valid
 T = total number of measurements

The Recycle and the Standard Methods samples are the only sample types that do not achieve the completeness criteria of 90% in Table 3.2. However, they approach 90 %, and are within one sample of passing this criterion.

As noted in Table 3.2, only 17 of the 340 long column samples were disqualified for faulty measurements (e.g., sample volume not noted). Additionally, three microsand samples fell below the 4 mg/L limit of detection for the EPA SS method, though these samples appear in the graphs as approaching zero concentration, or 100% removal.

Table 3.2 Completeness of Suspended Solids Analysis

Type or location	Total Samples	Voided Samples	Expected Completeness	Measured Completeness
Blanks	17	0	90%	100%
CERGRENE	101	0	90%	100%
Long	340	17	90%	95%
Recycle	45	5	90%	88.9%
Standard Methods	16	2	90%	87.5%

Of the 101 separate CERGRENE samples, none of the samples were voided. However, in lieu of incomplete information, when omissions in measurement could not be deduced, standard values were assumed. These values had to do with measured volumes of the CERGRENE column. The bottom of the column was assumed to be 960 mL, which did not vary noticeably when measured directly, and in fact should not have varied at all, as the bottom portion was filled to capacity. After the first few runs, it was decided more error was introduced by measuring than assuming the 960 mL value. The default bottom volume of 960 mL was used in calculating the upper chamber volume and percent removals, but the measured volume was used for actual SS concentration of the bottom effluent.

Due to faulty recording procedures, height measurements, which represents the volume of the top chamber in the CERGRENE columns, were not recorded for several individual CERGRENE runs. This measurement was not critical at the time of the laboratory analysis but became more critical during analysis of the settling velocities using CERGRENE's iterative matrix program. Where no height measurement was available, a value of 41.9 cm (16.5 in.) was used. This value is the mode for the 86 out of 101 samples for which a height measurement is available, with a mean of 41.4 cm (16.3 in.), a standard deviation of 1.7 cm (0.65 in.) and a coefficient of variance (CV) of 0.040. As the test proceeded, better control of the level in the CERGRENE columns was exhibited. For experiments 10 through 15, which are the only acceptable CERGRENE experiments, the mode was 41.9 cm (16.5 in.), the average was 42.1 cm (16.6 in.), with a tighter standard deviation of 1.3 cm (0.53 in.) and CV of 0.032 for fewer samples (31 of 40 samples). Measurements could only be made to the nearest eighth-inch, which implies a virtually identical mean and mode.

The error introduced by the lack of height measurements is minor in comparison to other sources. The major cause of variability in the SS analysis was the use of the microsand itself. During sample preparation, sand could be observed clinging to the filter housing, and was subsequently scraped onto the filter. This was not as apparent with the mixture, as the Neshaminy may have clung to some of the sand and reduced water tension of the sand to the filter housing.

Neshaminy soil tended to clog the filters for large volume CERGRENE samples. For this reason, 250 mL aliquots were obtained of Neshaminy CERGRENE samples from beakers with magnetic stirrers, and these aliquots were analyzed for SS. Thus filters were not overloaded for Neshaminy runs (where overloaded is defined by SM 2540 as exceeding 200 mg of residue). The aliquot method could not be used for microsand or mixture runs, as sand particles tended to be more discrete and a representative sample could not be obtained with magnetic stirrers as with the Neshaminy which formed a more colloidal mixture. Sample loading for the filters exceeded 200 mg for the CERGRENE columns. Thus the larger sand and mixture samples tended to overload the filters, which may have introduced considerable error in microsand CERGRENE runs.

Mixing Basin - Recycle

Three “recycle” samples were obtained immediately prior to filling the Long column. The known concentration in the mixing basin was 300 mg/L, so recycle concentrations should have centered around that number. The recycle concentration of each test was used as the t_0 of the Long column in lieu of averaging the initial measurements at each port in the Long column. The recycle samples were taken from the same pump that filled the Long column. The recycle concentration was thought to better represent the concentration delivered to the Long column. The average recycle concentration for all 15 test was 272 which represented less than a 10% loss overall from the known concentration.

Figure A-6 shows all recycle concentrations for all experiments. The data appear to be spread over a wide range of concentrations, but when viewed by soil type (Figure A-7), it becomes apparent that Neshaminy soil, with its higher percentage of clay and silt, yields tighter distributions around 300 mg/L, while the microsand tends to be much more widely distributed and unpredictable. This is due in part to the nature of the sand particles, which are discrete and dense, and may elude the sampling container or settle beneath the mixer. In addition, the SS analysis was much more robust for Neshaminy than for sand. Thus the mixed soil, with its combination of Neshaminy and sand, shows a distribution not quite as tight as Neshaminy, but not as widely distributed as sand.

Figures A-8 and A-9 show recycle concentrations by order of filling and depth of sampling, respectively. The recycle concentration distribution is closer to 300 mg/L for the experiments where the long column was filled first, and for the experiments where the height above the bottom of the basin was to 35 cm (14 in.) rather than 18 cm (7 in.). A second finding is that filling concentrations are closer to the known concentration when the intake is closer to the surface of the water in the basin. The first finding shows tighter distributions when the long column was filled first, which is probably a result of larger volumes of water providing better mixing. When the CERGRENE columns were filled first, enough water was removed from the basin to interfere with the mixing process. However, an analysis of variance showed no significant difference in recycle concentrations between media type, order of filling or intake depth.

Settleable Solids

The gravimetric settleable solids analysis (SM 2540F) entails first performing a SS analysis on a representative sample. In this experiment, settleable solids samples were taken the same way the Recycle samples were taken.

Figure A-10 shows the non-settleable solids concentration for this method for Neshaminy and mixture media. The settleable solids method was not performed on the microsand as insignificant concentrations of non-settleable solids were expected. The concentrations of the mixture medium is about half that of the Neshaminy, which is expected as the mixture contains half the mass of Neshaminy soils. An interesting result, however, is the tighter distribution of the mixture results, possibly due to a flocculent effect, where charged clay particles may cling to microsand particles and settle more predictably.

Laboratory Experiments 1-15

Concentration versus Time

Figures B-1 through B-30 show plots of the raw data for the long and CERGRENE columns for the 15 experiments. The first nine CERGRENE graphs are shown for completeness only. As mentioned previously, the inconsistency between CERGRENE columns makes it unadvisable to use the data from the first nine CERGRENE runs. Experiments 10 through 15, where one CERGRENE column was used repeatedly, show an increasing pattern in the graphs, as would be expected.

The graphs of the long column results show the pattern of settling for particles of each type. Note the rapid settling for the sand experiments, where concentrations at all ports quickly tail off to near zero. Neshaminy experiments exhibit a more gradual settling pattern, with the higher ports decreasing gradually, and the lower ports less so, as they receive the settled particles from the higher elevations. The mixed soil type shows an initial rapid settling of the sand particles, followed by the more gradual Neshaminy pattern. This becomes even more apparent in Figure B-31, which shows the results of the fifteen experiments on the Long column, averaged by soil type.

Long Column Shortcomings - Initial Concentration Gradient

An inherent problem in the design of the Long column is the lack of reliable uniformity in initial concentration (C_0). The height and volume of the column makes it difficult to deliver the sample quickly enough to ensure minimal settling of solids during the delivery time. Thus, depending on the density and particle size in the sample being delivered, a concentration gradient appears in the time zero measurements. This is compounded by the fact that simultaneous t_0 measurements were impossible to achieve in the Long column by hand (three people were performing the sampling). Because of the very nature of the sampling methodology, a lag will develop between completion of sample delivery and initial measurements, and between the port measurements themselves. A full minute may elapse between end-of-delivery and first sampling at port 8.

Figure B-32 shows port-by-port (represented by height above the column bottom) average concentrations for each soil type and each time interval. For a well mixed column, t_0 measurements should yield a straight line with zero slope, and a y-intercept equal to the recycle concentration. The slope of the t_0 line indicates the severity of the gradient. While the sand shows a severe lack of mixing, due to the size and density of the particles, the Neshaminy soil shows more uniform concentrations and exhibits better mixing. This is because Neshaminy contained clay particles which have lower specific gravities than sand and typically are not spherical in nature. The Neshaminy also took longer to settle with significant concentrations after one hour while the sand had settled out within five minutes. This problem has long been recognized as a shortcoming of the Long column, and causes the scatter that can be seen in the early measurements of more in-depth analysis.

In fact, concentrations for the lower Ports 5, 7 and 8, especially 7 and 8, during the test using the Neshaminy soil were probably demonstrating hindered zone settling and could even have been displaying compression zone settling. Concentrations were relatively flat throughout the test, except for an initial dip, and even began to exceed the known delivered concentration of 300 mg/L for ports 7 and 8 after one hour as demonstrated in Figure B 31.

CERGRENE Shortcomings - Lack of Repeatable Results

The precision of the SS concentration in the mixing basin can be calculated from the analysis of triplicate samples. The precision of the CERGRENE columns can be calculated from the duplication of a sample at a specified time.

Precision for duplicate analysis was estimated by calculation of the relative percent difference using the following equation:

$$RPD = ((C_1 - C_2) \times 100) / ((C_1 + C_2)/2) \quad (3-3)$$

where RPD = relative percent difference
 C_1 = the larger of the two observed values
 C_2 = the smaller of the two observed values

When three or more replicates are available, the relative standard deviation (RSD), instead of the RPD, was used as follows:

$$RSD = (s/y) \times 100\% \quad (3-4)$$

where: s = standard deviation, and
 y = mean replicate analysis.

The standard deviation is defined by:

$$s = \sqrt{\sum_{i=1}^n \frac{(y_i - \bar{y})^2}{n - 1}} \quad (3-5)$$

where:
s = standard deviation
 y_i = measured value of the i th replicate
 \bar{y} = mean of replicate measurements
n = number of replicates

For each run, a duplicate CERGREN column was tested and three Recycles were taken. The differences in these values is presented in Table 3.3.

Table 3.3 Duplicate Analysis for Recycle Concentration and CERGREN Columns

Test #	QA Run #	Withdrawal Height (cm)	Filling Sequence	Media	Recycle		CERGREN Duplicate	
					RPD (%)	RSD (%)	Duplicate Time (min)	RPD (%)
1	8	18	L/C	Neshaminy	- -	0.53	NA	No Duplicate
2	12	36	L/C	Mixture	26.1	- -	3	28.6
3	11	18	C/L	Mixture	- -	14.7	3	18.6
4	3	36	C/L	Neshaminy	- -	24.2	1	7.2
5	5	18	L/C	Neshaminy	- -	6.2	0	23.8
6	14	18	L/C	Microsand	2.6	- -	60	9.8
7	15	36	L/C	Mixture	- -	11.8	10	35
8	1	18	C/L	Microsand	- -	14.1	5	5.9
9	9	36	C/L	Mixture	- -	9.1	3	8.2
10	6	36	L/C	Neshaminy	- -	5.6	1	0.56
11	10	18	L/C	Mixture	- -	8.8	0	0.25
12	13	36	L/C	Microsand	- -	5.3	10	22.2
13	4	18	C/L	Microsand	17.8	- -	5	12.6
14	7	36	C/L	Neshaminy	4.9	- -	60	1.1
15	2	18	C/L	Microsand	- -	9.6	1	2.1

This data indicates that the variation of the recycle concentration for each test was random and not media driven (microsand, Neshaminy and mixture). This may be due in part to the

size of the samples taken (about 250 mL) and the force with which the sample bottles were filled by the pump (the same pump used to fill the Long column).

The duplicate analysis for the CERGRENE column tells a different story. During the first nine tests, four CERGRENE columns were used. For the remaining six tests, only one column was used. Here the CERGRENE columns behave randomly for the first nine tests, and then duplicate analysis improves dramatically as distinct patterns can be interpreted from the media being tested. The Neshaminy and mixture have better duplicates than the microsand. While the amount of data may not be large enough to state this finding with statistical validity, this observable result is expected. The percent recovery analysis of the “Standard Reference Material” indicated the microsand had the largest variation while the Neshaminy had the least with the mixture somewhere in between. That the performance of the CERGRENE columns in the last six test shows that the duplicate were better than the expected results from the SRM analysis may be due in part to the CERGRENE columns using larger volumes of sample.

As the recycle concentrations continued to behave randomly, the improved CERGRENE performance in the latter test was not due to enhanced technique of the testers as the experiment progressed. One column, instead of a several columns each with their own idiosyncracies, produced repeatable results. This duplicate analysis only compared the SS concentration and not settling rates.

Percent Removal Long Versus CERGRENE

Traditional methods of computing settling velocity distribution based on settling column data rely on a simple depth per time relationship. In the Long column, the depth measurements from each port in the Long column are divided by time of the sample to calculate the settling velocity distribution or the design overflow rate which can then be used in settling tank design. Though this computed number is in units of length per time (cm/s), it is not equivalent to a discrete particle settling velocity. The C_0 in the Long column are presumed to be uniformly distributed at all depths, however no direct measurement can be made to the length of the particles' flow path. Had a plug flow been introduced in the top of the column, the settling velocity computation would be more straightforward.

This design overflow rate was plotted versus the percent removal. For the Long column, percent removal is defined as the SS concentration at the port compared to the average recycle concentration for that run, which is the theoretical C_0 at every port. Though the actual C_0 at each port were obviously not equal to the recycle concentrations (see discussion on lack of well-mixed conditions), this is a necessary assumption to construct a plausible settling curve, and resulted in practical results with little scatter for the slower settling solids.

For the CERGRENE column, the overflow rate is compared to percent removal for each column of time greater than zero. Overflow rate is computed by dividing the distance an average particle traveled by the time measurement of the column. Thus, for each CERGRENE column, the number is computed by dividing one-half of the length of the upper portion of the water column (from the middle ball valve until the top water level) by the specific column's time, be it 1, 3, 5, 10 or 60 minutes. The C_0 in each column is assumed to be equal to the time zero

column's bottom portion concentration. Percent removal is defined to be each column's top portion concentration (computed by comparing to the bottom portion concentration) divided by the column's assumed C_0 .

Figures C-1 through C-9 show Long column results for experiments 1 through 9. The CERGREN results are not reliable and are therefore not shown. Figures C-10 through C-21 show long and CERGREN results for experiments 10 through 15. The shapes of settling curves are comparable for the two methods, the immediately obvious flaws are apparent in the sand experiments (12, 13, and 15). The Long column is overstating overflow rates for the fast settlers, as the right side of the Long column graphs should approach zero for increasing settling rates, and the CERGREN columns are under estimate removal rates, as they should approach 100% on the left side of the graphs. For the Long column, this shortcoming is due to the lack of adequate initial mixing. The assumption of C_0 being equivalent to average recycle concentration yields false concentration for the rapid settlers. For the CERGREN column, the very large volumes of analytes made it difficult to do the SS analysis for sand. Theoretically all the sand should have settled out at five and ten minutes and percent recovery should have been 100%. Losses of mass result in prediction of lower concentrations. Besides the problems with the SS analysis already discussed under *Completeness*, some sand particles may have been trapped in the ball valve mechanism. This is currently under investigation.

Matrix Iteration Process for CERGREN Columns

The CERGREN group of France (Lucas-Aiguier et al., 1997) developed a methodology to use the data from the small columns to produce settling velocity distributions. A spreadsheet application, "VICTOR", was developed which utilizes an iterative method to solve simultaneous equations, resulting in a matrix $M(i,j)$ which contains mass removed for each particular time interval i and pollutant j . Based on this matrix, a distribution of settling velocities may be constructed. A more complete description of the derivation is in Appendix G.

The nature of the CERGREN process sometimes results in certain points being in error. Thus a graph of $M(i,j)$ for a particular pollutant concentration, in our case SS, versus time, which should increase monotonically, may have discrete points which exceed the following temporal point. The software allows the user to choose either analysis of all points, which includes all data in the computation of the velocity distribution, or analysis with "suppression", which excludes points which do not show the expected increasing concentration in time. The choice of suppression or non-suppression is based upon several factors, but unless the points in question are significantly skewed to one direction, it will not have a severe impact on the resultant velocity distribution.

As discussed earlier, further analysis of CERGREN experiments 1 through 9 is not valid due to the inconsistencies between columns. Figure D-1 illustrates experiment 9, where the column order was randomized, and no consistent pattern can be seen in either graph. Suppression is not possible with this data, as no pattern can be inferred from the mass removal graph. This may be contrasted with Figure D-2, which shows the results from experiment 10, where one column was cleaned and reused for each time interval. Monotonically increasing mass removal values are seen, as well as a more varied velocity distribution.

Figure D-3 shows the results of experiment 11, utilizing all points. Figure D-4 shows the results after suppressing points 2 and 5, which fall outside of the expected pattern. Note the differences in the velocity distributions, especially in the slowest reaches, where the 3600 second point was suppressed. The basic shape of the distribution, however, remains the same.

Figure D-5 shows experiment 12, where suppression was not possible, because suppression would leave only 2 points for analysis. The shape of the velocity distribution, however, is similar to that of experiment 13 (Figure D-6), both of them being sand experiments. The third point in Figure D-6 could have been suppressed, but it does not fall far outside the curve, and thus is probably more useful being left in the analysis. Suppression of this point results in a sharper drop-off at the slower settling velocities.

Figures D-7 through D-10 illustrate experiments 14 and 15, with and without suppression. Note that the shapes of the velocity distributions remain similar whether or not points are suppressed.

VICTOR proves a useful tool for computing a settling velocity distribution for the CERGRENE columns. Care must be taken, however, in trying to compare these velocity results to the results from other types of analysis, which use different assumptions and computational techniques, and even different methods for deriving settling velocity distribution. Additionally, VICTOR would appear to work better with higher numbers of samples and time intervals. The capability of the software to track several pollutants could be a very useful for partitioning experiments, though this feature was not examined here.

Eckenfelder Analysis for Long Column

Use of Eckenfelder plots proved to be an inappropriate analysis for the media in Phase II. The Eckenfelder analysis is generally used to provide flocculent analysis. For the analysis to be successful, iso-concentration lines need to be developed from plotting concentration values for each sample depth (y coordinate) and time (x coordinate). The clay particles were not settling, and in fact concentration increased at the lowest port for several experiments at the one hour mark. This, as stated earlier, seemed typical of hindered or compaction zone settling. During the sand and mixture experiments the sand settled within a five minute time frame and exhibited properties of discrete settling.

Design Removal Comparison

Table 3.4 shows calculated overflow rates versus percent removals for the Long and CERGRENE columns for experiments 10 through 15. Calculations were identical to those used to develop the graphs in Appendix C, except that outlying CERGRENE points were deleted if the Victor algorithm suppressed the points automatically. Results from the Victor analysis were wildly divergent from the calculated results in Table 3.4, possibly due to lack of sufficient data points to effectively utilize the Victor tool. In fact, settling velocity results of Victor runs do not even show a noticeable difference between media. Comparisons of Long to CERGRENE results shows some similarities, though CERGRENE analysis is complicated by the lack of sufficient data points.

The calculated Stoke's Law settling velocities for ideally spherical sand at 15 °C ranged from 0.5 cm/s for 80 µm diameter sand to 12.6 cm/s for 400 µm. At 230 µm, the d_{50} value as calculated by the Coulter® LS Particle Analyzer for the microsand, the settling velocity was 9.3 cm/s.

Table 3.4 Comparison Predicted Removal between Long and CERGRENE Columns

Experiment (Media)	Percent Removed (%)	Overflow Rate (cm/s) Long [†]	r^2	Overflow Rate (cm/s) CERGRENE [‡]	r^2 (#pts)
10 (Neshaminy)	30	0.069	0.81	0.072	0.96 (5)
	50	0.0077		0.010	
	70	0.00086		0.0015	
11 (Mixture)	30	4.4	0.61	0.30	0.99 (3)
	50	0.14		0.0014	
	70	0.0046		0.0000069	
12 (Microsand)	30	100	0.64	100	0.22 (4)
	50	18		1.27	
	70	3.1		0.016	
13 (Microsand)	30	120	0.65	1.8	0.92 (4)
	50	20.		0.076	
	70	3.4		0.0032	
14 (Neshaminy)	30	0.014	0.43	0.61	0.82 (4)
	50	0.00059		0.094	
	70	0.000024		0.015	
15 (Microsand)	30	220	0.66	31000	0.90 (3)
	50	30.		30.	
	70	4.0		0.00028	

[†] Based on average recycle concentration. Points with calculated %Removal<0 were deleted.

[‡] Points removed by the Victor “suppression” algorithm were deleted, often yielding few points. Number of points used in the analysis is shown with the correlation coefficient.